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13. ABSTRACT (Maximum 200 words)

Work carried out under this grant is summarized. In particular, the prediction of a novel ferroelectric material $NaCaF_3$ is described and its predicted properties summarized. First principles calculations on a wide range of ionic molecular solids are summarized. These range from studies on halide perovoskites to work on alkaline earth silicates. In most cases very reasonable accord with experiment is achieved. One notable exception is the class of alkali cyanides which clearly require more sophisticated treatment. The basic theoretical approach is a combination of a Gordon-Kim modified electron gas theory with the quantum chemistry GAUSSIAN code to handle covalently bonded molecular ions. As indicated, this parameter free treatment reproduces experimental phase diagrams with good accuracy.

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Sincerely,

Dr. John R. Hardy

Studies on the Microwave Optics of Ionic Molecular Solids

Final Report

John R. Hardy

March 15, 2002

U.S. Army Research Office

DAAG55-97-1-0106

Department of Physics and Center for Electro-Optics
University of Nebraska-Lincoln
Lincoln, NE 68588-0111

INTRODUCTION

The current program is a continuation of our previous studies on the "computer engineering" of ionic molecular solids. The basic aim of the program is the predictions of physical properties by First Principles calculations entirely free from disposable parameters.

Our principal theoretical tool is the Gordon-Kim form of the modified electron gas approximation, supplemented by quantum chemistry for the treatment of covalently bonded molecular groups, e.g., SO_4^{2-}. Most recently this has been supplemented by the self-consistent atomic deformation model (SCAD) and full augmented plane wave band structure calculations. In addition, studies have been made on the phase diagrams of binary mixtures of different fluorides. One material we have particularly emphasized is sodium calcium trifluoride. While this has only been synthesized in the computer, its predicted properties are so interesting that actual physical synthesis could produce a material with extremely useful properties. Specifically, we find it to assume the lithium niobate structure with a ferroelectric polarization at ambient temperature comparable to barium titanate. This suggests that it is a candidate for ferroelectric applications which could be superior to conventional oxide-based systems. In particular, it is transparent well into the ultra violet (UV) and could, for example, provide a non-linear material for UV optics, as distinct from oxides which are opaque in this spectral range.

Since the abstracts of our relevant publications contain a full summary of each investigation, we shall use these interspersed with appropriate introductory material.

Studies on Mixed Fluorides

These are described in the following two abstracts. In one case, $KCaF_3$ is mixed with $RbCaF_3$, in the other the components are $NaMgF_3$ and $KMgF_3$.

As can be seen agreement between theory (Gordon-Kim) and experiment is good, in particular an observed eutectic point in the $KMgF_3$, $NaMgF_3$, phase diagram is reproduced by theory.

Structural Phase Transitions in Ionic Molecular Solids

This is a general review paper which discusses at length the basic principles which govern the origins of incommensurate phases in these systems. It brings together a wide range of our earlier results in order to exemplify these principles.

Structural Phase Transitions in Systems with Linear Molecular Ions

These papers discuss the order-disorder transitions in alkali azides, thiocyanates, cyanides and thallium azide. All of these compounds are either distorted NaCl or CsCl structures. The transitions involve hindered rotations of the linear ions producing a variety of high temperature phases, some of which while predicted theoretically, are pre-empted by melting in the real systems.

Studies on Mixed Fluorides Abstract

Pergamon

Materials Research Bulletin, Vol. 31, No. 9, pp. 1093-1099, 1996

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PHASE TRANSITIONS IN MIXED ALKALI CALCIUM TRIFLUORIDE SOLID SOLUTIONS

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(Refereed)
(Received April 22, 1996; Accepted May 20, 1996)

ABSTRACT

Both $KCaF_3$ and $RbCaF_3$ are known to undergo ferroelastic phase transitions, the former at temperatures near 550 K and the latter at 195 and 40 K. The two compounds comprise ends of the completely miscible solid solution $K_{1-x}Rb_xCaF_3$. Simulations of molecular dynamics have been performed for this solid solution, where Rb^+ ions were substituted for K^+ ions in $KCaF_3$ in varying concentrations of randomly distributed defects representing constitutional crossover to $RbCaF_3$. First-principles calculations were used to obtain the potentials between ion pairs in these samples; the pair potentials were used to calculate the temperature dependence of the interaxis angles which were used as markers for the polymorphic phase transition. The calculated transition temperature thus obtained decreases in a nearly linear fashion as a function of Rb^+ ion concentration. Experimental transition temperatures obtained from differential scanning calorimetry of actual samples agree well with the calculated temperatures for those compositions with transitions above room temperature.

KEYWORDS: A. fluorides, C. differential scanning calorimetry (DSC), D. phase transitions

Pergamon

Materials Research Bulletin 35 (2000) 341–349

Materials Research Bulletin

Polymorphic phase transitions in mixed alkali magnesium fluoride solid solutions

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(Refereed)
Received 17 May 1999; accepted 24 May 1999

Abstract

Phase transitions in the miscible solid solution $Na_{1-x}K_xMgF_3$ were examined over a wide range of compositions by computer molecular dynamics, X-ray diffraction, and thermal analysis in order to characterize the polymorphic phase transitions as a function of alkali-metal content. The pure $NaMgF_3$ composition has a single orthorhombic-to-cubic transition at 1038 K, but computer modeled compositions with K^+ partially substituted for Na^+ ions have at least two polymorphic transitions. The models also indicate that the transition temperatures decrease with increasing potassium content. Results from thermal analyses and from literature give similar results. Computer simulations, experimental data, and literature values all show a room-temperature transition for the composition around $Na_{0.65}K_{0.35}MgF_3$. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Fluorides; C. Differential scanning calorimetry (DSC); C. X-ray diffraction; D. Lattice dynamics; D. Phase transitions

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PII: S0025-5408(00)00232-4

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STRUCTURAL PHASE TRANSITIONS IN IONIC MOLECULAR SOLIDS*

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An overview is presented of our studies on the nature of structural instabilities in relatively complex ionic solids. These are based on parameter-free interionic potentials based on the Gordon–Kim modified electron gas formalism extended to molecular ions.

We describe the manner in which there emerge from these studies quite general concepts of "size" and "shape" as structural determinants. In particular, we discuss how these, and the approximate symmetries that they can produce, can provide a relatively simple structure-based explanation of the origins of incommensurate phases in these systems. However, we also emphasize that the existence of such symmetries does *not guarantee* an incommensurate phase. This can only be realized if long-range correlations are sufficiently strong to overcome random local disordering. Thus, either the molecular units are partially linked and/or there exist long-range Coulomb interactions between individual units.

Keywords: Lattice dynamics; Ionic molecular solids; Incommensurate structures

Perhaps the most interesting system is KSCN. Experimentally, this appears to assume a tetragonal structure just prior to melting. However, mircoscopically, it is found to consist of dynamically moving domains of the low-temperature orthorhombic phase. Theoretically, our molecular dynamics supercell is far too small to reveal this behavior. However, what we do observe is the onset of CNS^- flipping out of the basal plane. We argue that this is the origin of the moving domain walls producing the dynamically twinned structure observed experimentally.

One of other significant finding is that our combined quantum chemistry Gordon-Kim approach produces activation barriers for CN^- rotations that are far too high, indicating that a more sophisticated approach (e.g., SCAD) is necessary for these strongly polar ions.

More Sophisticated First Principles Studies

The first two investigations under this heading are applications of the self-consistent atomic deformation model (SCAD). In this model, localized atomic states centered on the respective ions are used. Each is then calculated self-consistently in the crystal field of the other ions. Thus, as the lattice is deformed, the ions deform in a self-consistent manner; the deformation at each site being consistent with the field at that site due to the other (deformed) ions. Hence, the overall charge distribution and total energy change are self-consistent.

In the first study, the method is applied to the alkali halide sequence with very reasonable results: in particular, polar motions produce Born effective charges in good accord with experiment as distinct from the simple Gordon-Kim result of unity in all cases.

In the second study, the method is applied to $NaCaF_3$ to examine the effect of this modification on the ferroelectric behavior of this system. Once again, the system is found to be ferroelectric with a well depth comparable to the Gordon-Kim value. Also, the compound remains metastable with respect to the constituents NaF and CaF_2.

Finally, we present a first principles study of the optical (linear and non-linear) properties of $KNbO_3$.

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach

This approach is that employed in our previous work on ionic molecular systems. The molecular ion charge density is calculated using the GAUSSIAN Quantum Chemistry package and it is then decomposed into individual atomic components which are employed in a Gordon-Kim derivation of all potentials external to the group. The internal motion is treated within the harmonic approximation using force constants generated by GAUSSIAN. For the monatomic cations, charge densities calculated from the tabulated wave functions are employed in the respective Gordon-Kim calculations.

Structural Phase Transitions in Systems with Linear Molecular Ions Abstract

PHYSICAL REVIEW B VOLUME 60, NUMBER 22 1 DECEMBER 1999-II

Molecular-dynamics study of phase transitions in alkali azides

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(Received 18 June 1999)

An account is presented of our studies of the order-disorder phase transitions in KN_3, RbN_3, and CsN_3. These are based on parameter-free interionic potentials based on the Gordon-Kim modified electron-gas formalism extended to molecular ions. We performed static structural relaxations and supercell molecular dynamics and predicted with reasonable accuracy the temperatures for the onset of the transitions. In particular, we address the question of how the N_3^- ions reorient to yield the transitions. We found the existence of NaCl-type high-temperature phases in disordered KN_3 and RbN_3 and argue that this restructuring is preempted by melting in these two systems. [S0163-1829(99)10541-1]

PHYSICAL REVIEW B VOLUME 62, NUMBER 5 1 AUGUST 2000-I

Molecular-dynamics study of phase transitions in alkali thiocyanates

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(Received 22 November 1999)

An account is presented of our studies of the order-disorder phase transitions in KSCN, RbSCN, and CsSCN. These are based on parameter-free interionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions. We performed static structural relaxations and supercell molecular dynamics and predicted with reasonable accuracy the temperatures for the onset of the transitions. In particular, we address the question of how the SCN^- ions disorder to yield subsequent structural transformations. We found high-temperature phases of average $Fm\bar{3}m$ symmetry for both KSCN and RbSCN. We argue that in reality the full appearance of these phases is preempted by melting. However, they are candidates for the twin boundaries which are observed in the high-temperature "average" tetragonal phases. The high-temperature phase of CsSCN was found to be of average $Fm\bar{3}m$ symmetry.

Computer Molecular Dynamics and Phase Transitions in Alkali Azides and Thiocyanates

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ABSTRACT

An account is presented of our studies of the order-disorder phase transitions in KN_3, RbN_3, CsN_3, KSCN, RbSCN and CsSCN. These are based on parameter-free inter-ionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions.

With these potentials we performed static structural relaxations and supercell molecular dynamics and predict with reasonable accuracy the temperatures for the onset of the transitions. In particular we address the question of how the N_3^- and SCN^- ions reorient to yield the transitions.

It was found that in case of azides we observed hindered rotations of the anions about all three crystallographic axes, in all three systems. However, in the thiocyanates only CsSCN yielded hindered rotations about all three axes. In KSCN and RbSCN the order-disorder transition appears rather to involve large amplitude librations of the SCN^- ions, primarily about the c axis.

Keywords: Azides; Thiocyanates; Ionic molecular solids; Phase transitions

Pergamon

Materials Research Bulletin 36 (2001) 2035–2041

Materials Research Bulletin

High-temperature phase transition in TlN_3

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(Refereed)
Received 9 January 2001; accepted 9 May 2001

Abstract

The phase transition in TlN_3 is simulated based on the potentials calculated from the Gordon-Kim modified electron gas model extended to ion molecular crystals. It is found that TlN_3 transforms into a cubic CsCl structure at high temperature due to the rotations of the N_3 ions. Above the phase transition the orientations of the N_3^- ions are random with four preferred orientations with respect to the cubic axes.

Keywords: D. phase transitions

Structural Transitions in NaCN and KCN

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†Department of Chemistry, University of Nebraska, Omaha, Nebraska 68182-0109*

Abstract. An account is presented of our studies of the order-disorder phase transitions in NaCN and KCN. These are based on parameter-free inter-ionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions.

We performed static structural relaxations and supercell molecular dynamics and reproduced two transitions known in each of these systems.

We also calculated upper bounds to the barrier of rotation of a cyanide ion in a ground state of NaCN and KCN and discuss possible shortcomings of our model.

More Sophosticated First Principles Studies Abstract

PHYSICAL REVIEW B VOLUME 61, NUMBER 17 1 MAY 2000-I

Calculation of electronic, structural, and vibrational properties in alkali halides using a density-functional method with localized densities

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(Received 7 December 1999)

A recently developed density-functional method based on localized densities is applied to calculate electronic, structural, and vibrational properties of 20 alkali halides with elements lithium through cesium and fluorine through iodine. Properties calculated include dissociation energy, lattice parameter, dielectric constant, elastic moduli, and phonon frequencies for the high-symmetry points of the Brillouin zone. Results are discussed and compared with experiment and other calculations.

Predicted Properties of $NaCaF_3$

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Abstract. More than a decade ago computer simulations based on Gordon-Kim potentials suggested that $NaCaF_3$ would be a ferroelectric compound if it could be formed experimentally. Recent attempts to form thin films of $NaCaF_3$ using pulsed-laser deposition have prompted us to carry out further theoretical studies of this material. Here we apply the self-consistent atomic deformation method to calculate electronic, structural and vibrational properties of $NaCaF_3$ and the constituent compounds NaF and CaF_2.

More Sophosticated First Principles Studies Abstract

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter 13 (2001) 8189–8195 PII: S0953-8984(01)25916-5

First-principles study on the optical properties of $KNbO_3$

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Abstract

We report our studies on the electronic structure and linear and nonlinear optical (NLO) properties of $KNbO_3$ using a first-principles method in the local density approximation (LDA). The calculated results for the refractive indices and second-harmonic-generation (SHG) coefficients agree well with experimental results. From decomposing the nonlinear susceptibility, we find that the primary contribution to the NLO behaviour comes from the hybridization of the O 2p and Nb 4d electron states. In addition, there are two different roles played by the O atoms because of their different distances from the Nb atom: thus we propose a possible way to enhance the SHG coefficients.

The following compounds have been studied: alkali nitrites; isomorphous $NaNO_3$ and $CaCO_3$; $RbNO_3$ and $CsNO_3$; $AgNO_3$; alkali percholorates; and alkaline earth silicates.

As before, this work is detailed in the following abstracts of the respective studies.

The nitrites are of particular interest insofar as the NO_2^- ion has a permanent dipole and thus, in the high temperature phases where these ions are in quasi-free rotation, they can couple to an applied microwave field and provide loss and optical dispersion. These compounds thus have potential applications for microwave optics. Of the other compounds, the silicates, in particular, are of geophysical interest - specifically their phase diagrams are the subject of controversy and our results may serve to settle this dispute.

PERSONNEL

Principal Investigator: Dr. John R. Hardy

Graduate Student/Postdoctoral Research Associate: Martin Ossowski

Visiting Scholar: Jianjun Liu

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach Abstract

PHYSICAL REVIEW B, VOLUME 63, 144105

Order-disorder phase transitions in KNO_2, $CsNO_2$, and $TlNO_2$ crystals: A molecular dynamics study

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(Received 5 January 2000; revised manuscript received 14 November 2000; published 16 March 2001)

The order-disorder phase transitions of KNO_2, $CsNO_2$, and $TlNO_2$ have been studied using parameter-free molecular dynamics simulation. It is found that the phase transitions in nitrites investigated are driven by the rotations of the NO_2^- ions about different axes together with displacements of cations and anions. We successfully reproduce the high-temperature phases of these nitrites, i.e., the NaCl-like structure for KNO_2 and CsCl-like structure for $Cs(Tl)NO_2$. Based on the investigation of the radial distribution function of the cations and anions, we explain why KNO_2 and $Cs(Tl)NO_2$ form quite different low-temperature phases.

DOI: 10.1103/PhysRevB.63.144105 PACS number(s): 64.60.Cn, 61.43.Bn, 64.70.Pf

Phys Chem Minerals (2001) 28: 586–590

ORIGINAL PAPER

Jianjun Liu · C.-G. Duan · M. M. Ossowski
W. N. Mei · R. W. Smith · J. R. Hardy

Simulation of structural phase transition in $NaNO_3$ and $CaCO_3$

Received: 30 January 2001 / Accepted: 11 May 2001

Abstract The order-disorder phase transitions in $NaNO_3$ and $CaCO_3$ are simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon–Kim modified electron gas formalism extended to molecular ions. We successfully reproduced the transition temperature T_c and the abnormally large c axis thermal expansion observed in experiment. The phase transitions in $NaNO_3$ and $CaCO_3$ were found to be initiated by ± 60 and $\pm 180°$ reorientation of the NO_3 and CO_3 ions about the c axis. The orientations of NO_3 and CO_3 ions are continuous with six preferred calcite-type orientations above the phase-transition temperature.

Key words Molecular dynamics simulation · Gordon–Kim potentials · Phase transition

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach Abstract

Simulation of Structural Transformation in Aragonite $CaCO_3$

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Abstract. The structural transformation in aragonite $CaCO_3$ is simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon-Kim modified electron gas formalism. We found two phase transitions in aragonite at high temperature.

CP535, *Fundamental Physics of Ferroelectrics 2000: Aspen Center for Physics Winter Wshp.*, edited by R. E. Cohen

Journal of Solid State Chemistry 160, 222–229 (2001)
doi:10.1006/jssc.2001.9226, available online at http://www.idealibrary.com on IDEAL®

Molecular Dynamics Simulation of Structural Phase Transitions in $RbNO_3$ and $CsNO_3$

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Structural phase transitions in $RbNO_3$ and $CsNO_3$ are studied by molecular dynamics. The simulations are based on the parameter-free potentials calculated from the Gordon–Kim modified electron gas formalism, extended to ionic molecular crystals. The microscopic mechanism of the structural phase transitions in $RbNO_3$ and $CsNO_3$ is revealed. It is found that the phase IV–III transition in $RbNO_3$ and the phase II–I transition in $CsNO_3$ are initiated by the in-plane and out-of-plane rotations of the NO_3 ions, and the phase III–II–I transitions in $RbNO_3$ are due to dilation along a trigonal axis of phase III, giving phase II a rhombohedral structure. © 2001 Academic Press

Key Words: molecular dynamics; Gordon–Kim potential; nitrate; phase transition; order–disorder.

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach Abstract

ELSEVIER

Journal of Physics and Chemistry of Solids 63 (2002) 409–414

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

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Molecular dynamics simulation of phase transition in $AgNO_3$

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Received 12 January 2001; accepted 30 April 2001

Abstract

Structural phase transition in $AgNO_3$ at high temperature is simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon–Kim modified electron-gas formalism extended to molecular ionic crystals. $AgNO_3$ transforms into rhombohedral structure at high temperature and the phase transition is associated with the rotations of the NO_3 ions and displacements of the NO_3 and Ag ions.

Keywords: A. Inorganic compounds; C. Ab initio calculations; D. Phase transitions

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Order–Disorder Structural Phase Transitions in Alkali Perchlorates

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Order–disorder structural phase transitions in alkali perchlorates $MClO_4$ (M = Na, K, Rb, Cs) are investigated using molecular dynamics simulation. The potentials in the simulations are based on the Gordon–Kim modified electron gas formalism extended to molecular ions. The simulations yield first-order phase transitions in perchlorates from low temperature orthorhombic structures to high temperature cubic NaCl structures. The perchlorate ions are found to be orientational disordered in the high temperature phases.

Key Words: alkali perchlorate; molecular-dynamics simulation; phase transition; Gordon–Kim potential; order–disorder.

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach Abstract

JOURNAL OF CHEMICAL PHYSICS VOLUME 116, NUMBER 9 1 MARCH 2002

Polymorphous transformations in alkaline-earth silicates

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Structural phase transitions in Ca_2SiO_4 and Sr_2SiO_4 are investigated by molecular dynamics simulations. The simulations are based on the potentials calculated from the Gordon–Kim modified electron gas formalism extended to molecular ions. We successfully reproduced the transition $\gamma-\alpha'_H-\alpha$ and $\beta-\alpha'_L-\alpha'_H-\alpha$ in Ca_2SiO_4, and the transition $\beta-\alpha'$ in Sr_2SiO_4. We find that the α'_L phase of Ca_2SiO_4 is an $a\times3b\times c$ superstructure of the α'_H phase, while the α'_H phase has a β-K_2SO_4 structure, and the α phase of Ca_2SiO_4 has a disordered structure with space group $P6_3/mmc$. [DOI: 10.1063/1.1446043]